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# PATENT SPECIFICATION

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NO DRAWINGS

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**Int. Cl.:**—D 06 m // D 01 f

## COMPLETE SPECIFICATION

### Improvements in and relating to the Modification of Cellulose Fibres

We, COURTAULDS LIMITED, a British Company of 18 Hanover Square, London, W.1, (formerly of 16, St. Martin's-le-Grand, in the City of London, England) do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to the modification of fabrics containing cellulose fibres and other forms of cellulose fibres by reaction with dialdehydes.

It has been proposed to modify the properties of cellulose by reaction with a dialdehyde, for example, glyoxal or glutaraldehyde. Thus the crease-resistant properties of the fibres may be increased and the water-imbibition reduced. However, we have found that a drawback associated with most of these treatments is that the beneficial effect of the modification diminishes with successive washes and that the cellulose material is frequently discoloured and tendered. These latter defects are particularly noticeable when more than 4 per cent by weight of glyoxal is taken up by the fibres.

We have now found a method of improving the wash fastness of the properties derived from the treatment with dialdehydes and, where it is important, mitigating the tendering and the discolouration of the fibres treated with glyoxal, even when 4 per cent by weight or more of dialdehyde is retained by the fibres.

According to the present invention, a process for modifying cellulose fibres comprises impregnating the fibres with a dialdehyde and a compound having 1 or at most 2 functional groups capable of converting a hemiacetal into an acetal; and subsequently drying and heating the fibres to a temperature above 100°C.

We consider that dialdehydes react with cellulose to crosslink the cellulose molecules with the formation of two hemiacetal groups. The reaction is represented by the equation



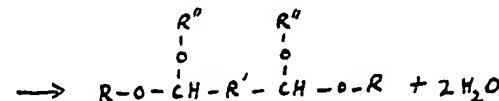
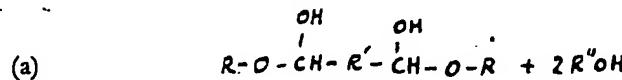
where ROH is a cellulose molecule and OHC-R'-CHO the dialdehyde.

Hemiacetal groups are easily hydrolysable under the conditions obtaining in domestic laundering, and this, we think, is the explanation of the impermanence of the modifications resulting from the simple reaction of dialdehydes and cellulose.

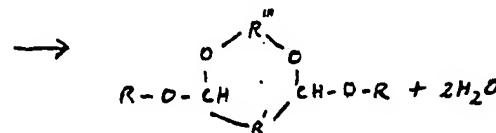
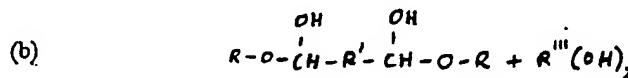
The stability of the crosslinks can be significantly improved by converting the hemiacetal groups to acetals and this can be achieved by reacting alcohols or aldehydes with the primary reaction product of a dialdehyde and cellulose.

This reaction is formulated in any of the equations

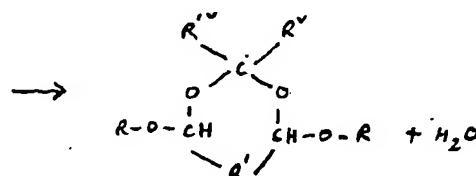
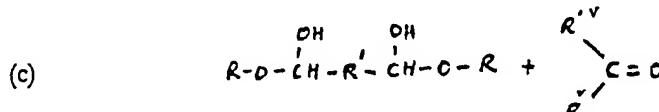
- 30      Hemiacetal groups are easily hydrolysable under the conditions obtaining in domestic laundering, and this, we think, is the explanation of the impermanence of the modifications resulting from the simple reaction of dialdehydes and cellulose.
- 35      The stability of the crosslinks can be significantly improved by converting the hemiacetal groups to acetals and this can be achieved by reacting alcohols or aldehydes with the primary reaction product of a dialdehyde and cellulose.
- 35      This reaction is formulated in any of the equations



where  $R''$  is alkyl,  $R''OH$  is therefore a monohydric alcohol.



where  $R'''$  is an alkylene group and  $R'''(OH)_2$  is a glycol.



where  $R''$  is alkyl or hydrogen and  $R''^v$  is methyl or hydrogen. The compound  $R''COR''^v$  is therefore an aliphatic ketone or aldehyde.

Whilst it is a feature of this invention that the dialdehyde and the compound capable of forming an acetal may be reacted simultaneously with the cellulose, we prefer the process in which the dialdehyde and cellulose are reacted and the product dried before it is impregnated with the acetal-forming compound, particularly where the latter compound is reactive to cellulose.

The reaction of the dialdehyde and cellulose does not require catalysis. The dialdehyde is applied as an aqueous solution and the physical conditions of the application and any step of removing the excess solution from the cellulose should preferably be governed so that the fibres retain from 4 per cent to 10 per cent, based on the weight of the dried fibres, of the dialdehyde. The aqueous solution should have a pH in the range 3 to 8, preferably 5 to 6, to avoid fully the disadvantages of degradation or discolouration of the cellulose due to the dispersion being too acid or too alkaline.

The reaction of the acetal-forming compound with the hemiacetal-containing cellulose requires catalysis and the compound should be applied to the cellulose as an aqueous solution, subject to the same pH limitations imposed on the dialdehyde/cellulose reaction. The catalyst used is a metal salt which is soluble to the extent of at least 0.3 gram mole per litre in water at 20°C. at pH 5 and is zinc sulphate or a salt of a metal of Group II of the Mendeleef Periodic Table with a monobasic acid

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which is ionised to the extent of at least 50 per cent if in normal aqueous solution at 18°C.

The salts may be salts of magnesium, the alkaline earth metals (i.e. calcium, barium and strontium), cadmium or zinc with the monobasic inorganic acids indicated. Salts of magnesium and, in somewhat less measure, salts of calcium are preferred.

The monobasic acid is preferably an inorganic acid and may be hydrochloric, hydrobromic, hydriodic, nitric, perchloric or thiocyanic acid.

Specific salts which may be employed as catalysts for the purpose of the present invention include the following:

	Invention include the following:	
10	Magnesium chloride, bromide or iodide	10
	Magnesium nitrate or perchlorate	
	Calcium chloride, bromide, iodide, nitrate or perchlorate	
	Strontium chloride	
	Barium chloride	
15	Cadmium chloride	15
	Zinc chloride, nitrate or sulphate	
	Magnesium boronate sulphate	

The conditions of retained reactant, pH range and catalyst imposed on the first and second stages of the two stage process should be simultaneously imposed in the one stage process.

The process may be applied to textile fabrics containing cellulose fibres; they may be woven or knitted fabrics or the so-called non-woven fabrics. The fabrics may consist wholly of cellulose fibres or in part of those fibres and in part of other fibres, but in the latter case it is preferred that the cellulose fibre content should not be less than 35 per cent by weight.

The process may also be applied to loose fibres. The cellulose fibres may be natural fibres such as cotton, sisal, flax, hemp, jute or ramie, or regenerated cellulose artificial fibres, for example those made by the viscose, cuprammonium, or nitrate process, or by the saponification of fibres of cellulose esters, for example cellulose acetate.

The regenerated cellulose fibres may be in the form of staple fibres or continuous filaments and these may be in the form of yarns or of tows i.e. relatively large substantially untwisted bundles of continuous filaments. Regenerated cellulose filaments may be such as have never been dried.

The dialdehyde is preferably glyoxal but glutaraldehyde, succinaldehyde and hydroxy-adipaldehyde are other examples of useful compounds. In the past we have found that technical grades of glyoxal solutions discoloured and weakened the cellulose fibres to which they were applied. We have found, more recently, that purer glyoxal solutions, i.e. solutions containing less than 5 per cent by weight of impurities, do not give rise to these colour-forming reactions to the same extent and their use is preferred in this process. It so happens that the technical grades contain oxidants and aldehydic impurities, but we are unable to attribute the colour-forming reaction to any specific impurity.

The acetal-forming compound is preferably an aldehyde, for example, formaldehyde, acetaldehyde or acrolein. Formaldehyde is particularly useful because of its cheapness, availability and efficient reactivity in this invention. The acetal-forming compound may be an alcohol or glycol, but these substances are less reactive than the aldehydes and, therefore more severe and stringent process conditions may be necessary to obtain the same modification.

The acetal-forming reaction requires the application of heat to the dried fibres. Thus in the second stage of the two-stage process or in the single stage process, the impregnated fibres are dried and heated above 100°C. The steps of drying and heating can be separated, for example by allowing the fibres to dry below 100°C. and subsequently heating the fibres. Otherwise, the fibres may be dried and heated in a continuous process in which the steps are merged. Thus the fibres may be heated by contact with a heated fluid or solid surface, for a time long enough to dry the fibres and complete the reaction. Temperatures of from 140°C. to 180°C. are preferred for completing the reaction.

60 A major benefit of the use of the metal salt catalysts during the heat-treatment of the fibres, is that the tendency to discolouration of the fibres, resulting from the use of an impregnating solution having a pH at the upper end of the preferred range, say 8, is reduced or eliminated completely. Magnesium chloride is very efficient in this respect.

We prefer that the fibres take up from 4 per cent to 10 per cent by weight

(based on the weight of the dry fibres) of the dialdehyde. This can be controlled by the concentration of the dialdehyde in the applied dispersion and the amount of liquid which the impregnated fibres are allowed to retain. For example, to impregnate fibres with 4 per cent of dialdehyde, the fibres can be immersed for a short period in a solution containing 4 per cent of dialdehyde and then mangled or centrifuged so that the fibres contain an equal weight of liquid. We have found that the dialdehydes are substantive to cellulose to such a degree that dilute solutions containing say 2 per cent of dialdehyde and retained by the centrifuged fibres in a weight equal to that of the dry fibres, have caused a 4 per cent pick up of dialdehyde. However, this result is only achieved by prolonging the contact of fibres and impregnating solution, and is similar in this respect to certain dyeing processes in which dye-bath exhaustion is achieved slowly.

In theory, the greatest gain in wash-fastness will result when two equivalent proportions of the acetal-forming compound are reacted with every molar proportion of reacted dialdehyde. Significant gains are to be had even when less acetal-forming compound is reacted, but at least 1 equivalent proportion must be used if the gain is to be substantial. This minimum required take-up in grams/100 gm of fibres of acetal-forming compound may be calculated from the formula:

$$X \times Y$$

where X is the equivalent weight of the acetal-forming compound and Y is the number of gram-molecules of dialdehyde reacted with 100 gms of fibres. However, it can happen, particularly when the acetal-forming compound is an aldehyde, that the take-up amount of that compound required to achieve the maximum stabilisation of the cellulose/dialdehyde product is greater than that theoretically required to convert the hemiacetal groups to acetals. This can arise from any one of a number of causes. For example, when, instead of a single aldehyde molecule reacting with a pair of hemiacetal groups according to Equation (c), the latter groups are reacted with and connected through a polymer of the aldehyde. Such polymeric aldehydes, or polyoxo-alkylenes, fulfil only the function of the monomeric aldehyde and can account for the larger than theoretical quantity of aldehyde sometimes required. Again, if the acetal-forming compound has a significant volatility under the conditions of the process, it may be necessary to allow for losses by impregnating the cellulose with more than the required amount of the compound.

The amount of acetal-forming compound taken up by the cellulose may be controlled by the same methods employed to regulate the take-up of the dialdehyde.

In the one stage process, in which the dialdehyde and acetal-forming compound are applied simultaneously to the cellulose, the ratio of reactants taken up by the cellulose is, in general, similar to the ratio existing in the impregnating solution.

The invention is illustrated by the following Examples.

The mechanical features of all Examples were identical and a single fabric quality was used throughout. The variables in the examples are the quantity and quality of the dialdehyde and quantity of the acetal-forming compound and the catalyst.

The fabric was an all-filament viscose rayon construction having the following properties:

Weave : plain  
Warp : yarn denier 100; number of filaments 51; 76 ends per inch  
Weft : yarn denier 120; number of filaments 33; 80 picks per inch

The processing conditions common to Examples 1 and 3 were that the cloth was padded with dialdehyde during 5.6 seconds in passing through a bath containing a 10 per cent aqueous solution of the dialdehyde at 0.4 feet/second (or 12.19 cm/second). The solution was maintained at 20°C. and controlled for pH. The impregnated fabric passed from the bath to a double immersion, double-nip, pad-mangle to reduce the quantity of retained liquor to 85 per cent by weight based on the weight of the dry fabric. From the mangle, the fabric was led onto a pin-stenter and there dried to width in 15 minutes at 80°C. The recently dried fabric was then padded once again in a bath containing an aqueous solution of the acetal-forming compound and a catalyst, at the same rate as for the first padding. The padding bath was controlled at a temperature of 20°C. and a pH characteristic of the example. Allowed to retain only 85 per cent by weight of the second padding solution, the fabric was once more dried to width on a stenter before being cured at 160°C. for 5 minutes. An interval of 10 minutes was allowed before the fabric was scoured with a 2 per cent soap solution at 60°C., rinsed and dried to width at 80°C.

Examples 2, 4 and 5 to 8 employed a single padding bath, the fabrics being treated thereafter in the same way as the twice padded fabric of Example 1.

The fabrics of all Examples were submitted to a number of tests both during the treatment and after. These tests were standard through the series and are, therefore, comparable. A Hoover (Trade Mark) washing machine was used in the tests to examine the extent to which the beneficial properties conferred on the fabric by this invention withstood ten washing cycles in a domestic washing machine. Each cycle comprised washing a 4 lb. (or 1.81 kg) load for 15 minutes at 60°C. with 2 gm/litre of soap, followed by a rinse, spin-dry and press. After the tenth cycle, samples were rinsed twice, spin-dried, pressed and conditioned at 65 per cent R.H. Fabrics were also submitted to a cotton wash (55 minutes at 95° to 100°C.) as described in B.S. 1118 and the properties measured once again. The results from all these tests are recorded in the following Table.

The remaining details of the processes employed are described under the headings of individual Examples.

#### EXAMPLE 1

15 The dialdehyde solution contained glyoxal at a pH of 4.4. The solution was made up from 99 per cent pure glyoxal monohydrate.

The second padding bath contained 5 per cent formaldehyde and 5 per cent magnesium chloride hexahydrate at a pH of 6.

#### EXAMPLE 2

20 The process of Example 1 was reduced to a one-stage padding operation by adding 5 per cent formaldehyde and 5 per cent magnesium chloride hexahydrate to the glyoxal bath. The pH was adjusted to 6.

#### EXAMPLE 3

25 The glyoxal bath of Example 1 was replaced by a liquor containing an equivalent amount of a technical grade of glyoxal supplied at a 30 per cent solution. The pH, originally 1.3, was adjusted with NaOH to 4.4. The second padding solution was that used in Example 1.

#### EXAMPLE 4

30 The process was that of Example 2, except that a technical grade of the padding solution was adjusted to 6 from 1.5, with NaOH.

#### EXAMPLE 5

As for Example 2, but omitting the formaldehyde and MgCl<sub>2</sub>, 6H<sub>2</sub>O from the padding solution.

#### EXAMPLE 6

35 As for Example 4, but omitting the formaldehyde and MgCl<sub>2</sub>, 6H<sub>2</sub>O from the padding solution.

#### EXAMPLE 7

As for Example 4, but omitting the formaldehyde.

#### EXAMPLE 8

40 As for Example 1, but both padding solutions comprising water at pH 6 and no reactants.

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TABLE

Example No.	State of fabric A = unscoured B = scoured C = washing m/c tested D = cotton washed	Fabric properties							
		% water imbib.	% bound reagents	% crease recovery		(lb.) warp strength		% shrinkage	
				warp	weft	tear	tensile	warp	weft
1	A	28	—	91	91	2.50	40.4	—	—
	B	30	6.3	92	90	—	—	—	—
	C	—	—	93	92	2.87	40.0	0.2	2.5
	D	32	—	90	85	3.06	37.5	0.1	1.3
2	A	30	—	93	84	1.48	34.2	—	—
	B	32	5.4	—	—	2.98	33.4	—	—
	C	—	—	—	—	—	—	—	—
	D	34	—	83	73	2.65	27.6	0.4	1.9
3	A	29	—	91	86	0.60	18.3	—	—
	B	—	4.1	—	—	—	—	—	—
	C	32	—	84	83	0.72	20.4	*	*
	D	—	—	86	81	0.49	15.0	*	*

TABLE—*continued*

Example No.	State of fabric A = unscoured B = scoured C = washing m/c tested D = cotton washed	Fabric properties						% shrinkage warp weft	
		% water imbib.	% bound reagents	% crease recovery		(lb.) warp strength			
				warp	weft	tear	tensile		
4	A	33	—	90	84	0.92	20.0	—	
	B	—	4.5	—	—	—	—	—	
	C	30	—	84	81	1.43	23.1	*	
	D	—	—	79	76	0.98	23.2	*	
5	A	29	—	91	88	2.50	40.2	—	
	B	85	0.2	65	53	3.32	41.8	—	
	C	—	—	—	—	—	—	—	
	D	80	—	63	54	3.06	45.5	6.4	
6	A	38	—	81	81	2.11	37.2	—	
	B	70	0.3	64	53	2.38	44.5	—	
	C	—	—	—	—	—	—	—	
	D	79	—	—	—	3.10	42.2	3.6	

TABLE—continued

Example No.	State of fabric A = unscoured B = scoured C = washing m/c tested D = cotton washed	Fabric properties							
		% bound reagents	% crease recovery		(lb.) warp strength		% shrinkage		
			warp	weft	warp	tear	warp	weft	
7	A	31	—	89	88	1.08	24.5	—	—
	B	36	4.9	90	84	—	—	—	—
	C	85	—	54	49	2.89	34.6	3.3	8.7
	D	91	—	57	44	2.76	38.0	6.1	9.3
8	A	88	—	50	46	3.94	34.0	—	—
	B	87	—	54	48	4.20	39.1	—	—
	C	83	—	51	50	2.91	39.7	2.0	10.4
	D	85	—	55	47	2.34	46.3	6.0	7.2

\* Sample tore during washing. No shrinkage figures available.

Examples 1 to 4 demonstrate the utility of the invention. Examples 5 to 7, none of which accord with the invention, are included to show the disadvantages of omitting the acetal-forming compound from the process. Example 8 gives the properties of the fabric which has been through the wet treatments and heat treatments of Example 1, but in the absence of reactants.

It will be seen from the Table that the results from the fabric treated according to Example 1 are consistently the best in all tests and that the group, Examples 1 to 4, shows distinct advantages over the remaining Examples. Attention is drawn to the good washing fastness of the excellent crease-recovery properties conferred by the process of this invention and the relatively small loss of tear strength and augmented tensile strength resulting from the process of Examples 1 and 2. The crease-recovery properties of the wet fabrics are also much improved. It is a feature of the treated fabrics of Examples 1 to 4 that they have a resilient nature. Not only do they recover well from creasing, but they do this very rapidly. A treated fabric sample, crushed in the hand, springs to a more open configuration when the hand is opened, quite unlike the sluggish response of the untreated fabric to this test. The poorer fabric strengths resulting from the processes of Examples 3 and 4 are directly attributable to the technical grade of glyoxal used in these processes. The low-water imbibitions of fabrics issuing from Examples 1 to 4 are noteworthy also as helping the easy-care characteristics of the fabrics.

Examples 3 and 4 were discoloured and the discolouration was permanent throughout the washing tests. Examples 6 and 7 were discoloured before scouring, but the colour diminished during the scouring and the machine washing test and almost disappeared in the cotton wash samples.

WHAT WE CLAIM IS:—

1. A process for the manufacture of crosslinked cellulose fibres, comprising impregnating and reacting cellulose fibres with an aqueous solution of a dialdehyde at a pH of from 3 to 8 to form a cellulose/dialdehyde adduct containing hemiacetal groups and reacting the adduct with an aqueous solution of a reactant having 1 or at most 2 functional groups capable of converting hemiacetal groups to acetal groups in the ratio of at least 1 equivalent proportion by weight of the reactant per molar proportion of reacted dialdehyde, at a pH of from 3 to 8 and in the presence of a catalyst which is a metal salt soluble to the extent of at least 0.3 gram mole per litre in water at 20°C at pH 5 and is zinc sulphate or a salt of a metal of Group II of the Mendeleef Periodic Table with a monobasic acid which is ionised to the extent of at least 50 per cent if in normal aqueous solution at 18°C, and subsequently drying and heating the fibres to a temperature above 100°C.
2. A process as claimed in Claim 1, in which the fibre is impregnated with a single aqueous solution containing the dialdehyde, the reactant and the catalyst.
3. A process as claimed in Claim 1, or 2 in which the reactant is an aldehyde or an alcohol.
4. A process as claimed in Claim 3, in which the reactant is formaldehyde.
5. A process as claimed in any preceding claim in which the dialdehyde is glyoxal containing less than 5 per cent by weight of the impurities which normally contaminate technical grades of glyoxal solutions.
6. A process as claimed in any preceding claim conducted at a pH of from 5 to 6.
7. A process as claimed in any preceding claim in which the adduct and the reactant are heated to from 140°C to 180°C during their reaction.
8. A process as claimed in any preceding claim in which the cellulose fibres are impregnated with from 4 per cent to 10 per cent by weight of the dialdehyde, based on the weight of the dry fibre.
9. A process as claimed in any preceding claim in which the catalyst is magnesium chloride.
10. A process as claimed in Claim 1 in which the cellulose fibre is first impregnated with an aqueous solution of glyoxal containing less than 5 per cent by weight impurities at a pH of from 5 to 6, so that the impregnated fibre occludes between 4 per cent and 10 per cent of glyoxal based on the weight of the fibre, drying the impregnated fibre to form the cellulose-dialdehyde adduct and subsequently impregnating the adduct with an aqueous solution of formaldehyde and magnesium chloride and heating the impregnated adduct to a temperature between 140°C and 180°C to form crosslinked cellulose fibres containing acetal groups.
11. A process as claimed in Claim 1 carried out substantially as described in any one of the Examples 1 to 4.

J. Y. & G. W. JOHNSON,  
Furnival House,  
14-18, High Holborn,  
London, W.C.1.  
Chartered Patent Agents,  
Agents for the Applicants.

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